

NCEM Proposal Title: “Surface and interfacial structures of nanocrystals”

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1) Scientific motivation for your project: The atomic structure of nanoparticle surfaces is of great importance for catalysis, yet poorly understood. The goal of this study is to develop a technique to reconstruct the 3-D atomic structure of the surface and interface of individual supported nanoparticles using a combination of geometric phase analysis, single particle nano-probe diffraction and simulation. In each case, state-of-the-art structure determination will compliment the high-resolution imaging to provide a framework for the analysis of nanoparticle surface structures through electron microscopy. The goal of this study is to develop a technique to reconstruct the 3-D atomic structure of the surface and interface of individual supported nanoparticles using a combination of geometric phase analysis (GPA) [1], single particle nano-probe diffraction (NPD) and simulation [2]. The atomic structure of nanoparticles' surfaces is of immediate use in understanding the surface chemistry of supported nanoparticles that form the basis of the multi-billion dollar catalyst industry.

2) Describe your experimental plan (including sample preparation, planned microscopy techniques & analysis): The starting point of this study is a unique sample preparation technique that consists of making thin and pristine single crystal TiO₂ surfaces (Figure 1) onto which nanoparticles can be loaded repetitively on the same plane of TiO₂. In this cross-sectional geometry, the electron beam travels only through the nanoparticle thus eliminating any interference effects with the substrate (Figure 2). Further, by eliminating the polymeric materials used in conventional cross-sectional TEM sample preparation, a high signal to noise ratio is achieved in the diffraction patterns. Since the particles are firmly attached to the substrate they pose no risk to environment, health and safety from exposure to engineered nanoparticles. We only anticipate examining one size of Au nanoparticles and the samples will be prepared and pre-screened in a microscope at UIUC. The dominant epitaxies observed with Au on TiO₂ are:

Au(111) || TiO₂(110)

Au(224) || TiO₂(110)

Au(200) || TiO₂(110)

The lattice spacings of Au (222) – 1.44 Å, Au (224) – 0.83 Å and Au (200) – 2.04Å are thus easily resolvable with the capabilities of both TEAM instruments at NCEM. Further, since delocalization in the TEAM microscopes is minimized; even a 0.05 Å change in lattice spacing should still be resolvable with confidence. We intend to use the TEAM microscope for high resolution imaging and nanoprobe diffraction sessions at NCEM and then perform the simulations at our home institution.

3) Prior work specific to this project and need for NCEM's unique or advanced facilities: Figure 3 shows a HRTEM image of a gold nanoparticle taken at the user's institution using a JEOL 2010FEG. It can be seen that the surface and interface atoms of the gold nanoparticle appear fuzzy due to microscope's aberrations and the consequent electron wavefunction delocalization. However, to verify the results from the coherent diffraction experiments and simulation, changes in lattice positions of the order of

0.05 Å need to be resolved with confidence. This can be achieved with GPA provided the image has a much higher quality. Therefore a microscope with much better point-to-point resolution as well as reduced delocalization is sought. The TEAM microscope is ideally suited to this need. The higher quality images can facilitate the measurement of changes in atomic positions of the order of ~0.05 Å using GPA.

4) *Microscopy experience of primary researcher:* The user has over 300 hours of hands on TEM experience and is proficient with JEOL 2010 FEG, JEOL 2010 LaB6, JEOL 2100 LaB6 and Philips CM-12 microscopes.

References:

[1] “Quantitative measurement of displacement and strain fields from HREM micrographs”, M.J.Hytc, E.Snoeck, R.Kilaas, Ultramicroscopy 74, 131-146 (1998)

[2] “Coordination-dependent surface atomic contraction in nanocrystals revealed by coherent diffraction”, W. J. Huang, R. Sun, J. Tao, L. D. Menard, R. G. Nuzzo & J. M. Zuo, Nature Materials 7, 308 - 313 (2008)

[3] “Low-temperature oxidation of CO over gold supported on TiO₂, alpha-Fe₂O₃ and Co₃O₄”, M.Haruta, S.Tsubota, T.Kobayashi, H.Kageyama, M.J.Genet, B.Delmon, Journal of catalysis 144, 1, 175-192 (1993)

Figures:

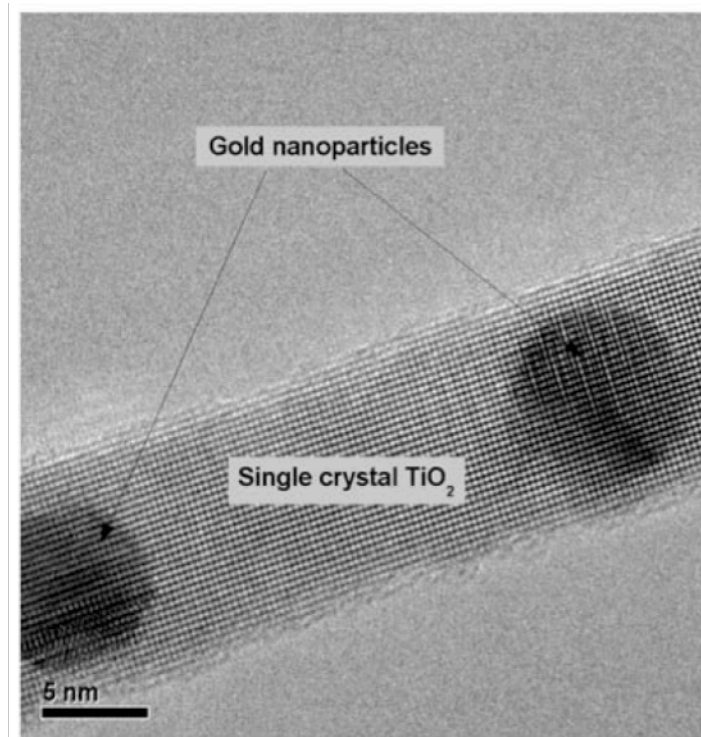


Figure 1: Thin and pristine single crystal TiO_2 (110)

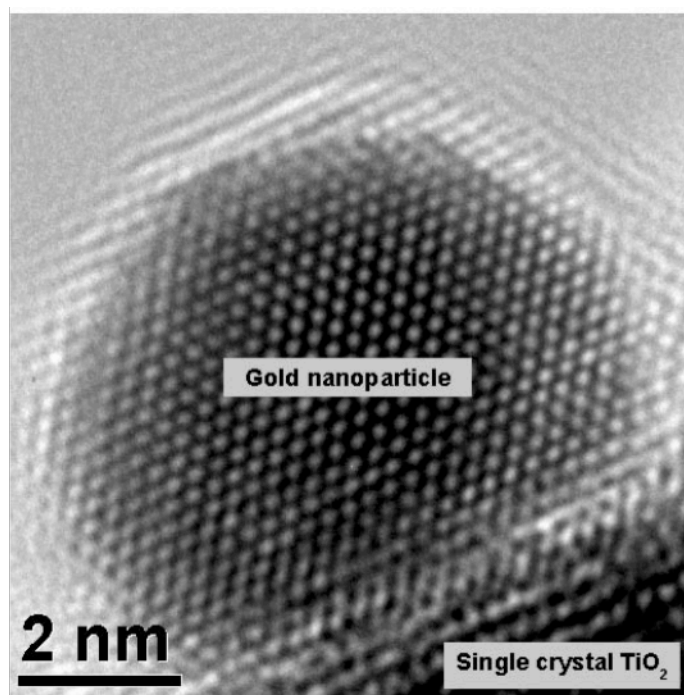


Figure 2: Au nanoparticle supported on Single crystal TiO_2 (110)

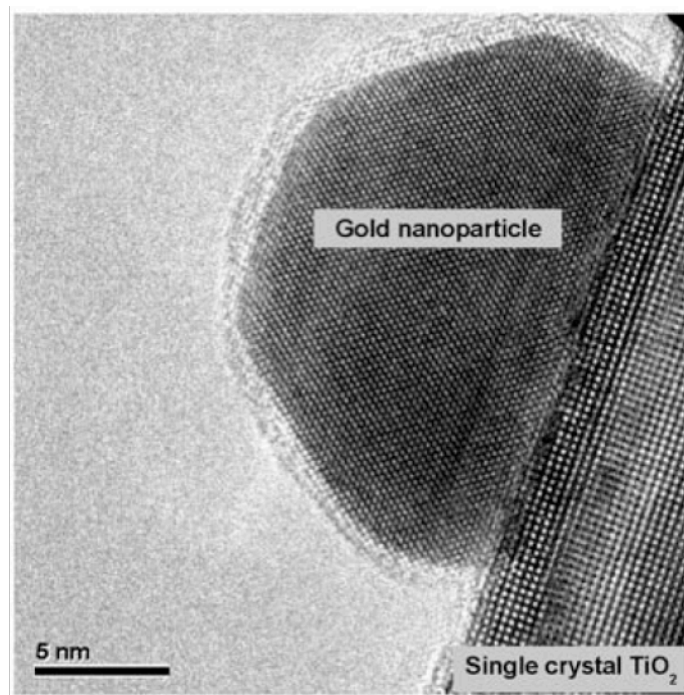


Figure 3: HRTEM image showing the surface and interface of Au- TiO_2 (110)